United States Patent Office

3,682,713
Patented Aug. 8, 1972

1

3,682,713

PROCESS FOR APPLYING PROTECTIVE COATINGS ON ALUMINUM, ZINC AND IRON

Christian Ries, Cologne-Kalk, and Günter Stolzenfels, Hurth-Efferen, Germany, assignors to Gerhard Collardin G.m.b.H., Cologne-Ehrenfeld, Germany

No Drawing. Filed June 25, 1970, Ser. No. 49,925
Claims priority, application Germany, June 26, 1969, P 19 33 013.3
Int. Cl. C23f 7/00
U.S. Cl. 148—6.14 R 13 Claims

ABSTRACT OF THE DISCLOSURE

A process for applying a protective coating on aluminum, zinc and iron under substantially identical operating conditions which consists essentially of applying to the metal surfaces of aluminum, zinc and iron of a complex fluoride coating solution free from chromic acid, phosphoric acid and oxalic acid having a concentration of from 0.1 to 15 gm. per liter, based on the metal content, of complex fluorides of metals selected from the group consisting of boron, titanium, zirconium and iron, from 0.1 to 10 gm. per liter of free fluoride ions and from 0.5 to 30 gm. per liter, calculated as sodium m-nitrobenzene sulfonate, of an oxidizing agent, at a pH of from 3.0 to 6.8 for a time sufficient to form a coating. The applied coatings can be post-passivated with solutions containing chromic or phosphoric acids.

THE PRIOR ART

It is known to apply protective coatings by means of acid solutions to steel and zinc or iron with zinc galvanized surfaces, to improve the corrosion protection and the adhesion of paint, varnish and plastic coatings. Previously there was applied to steel surfaces, generally phosphatizing solutions and to zinc surfaces phosphatizing solutions and chromating solutions. However, not in all cases could satisfactory results be obtained with these processes. The phosphate coatings, which in themselves give good corrosion protection, have the disadvantage of poor varnish adhesion if a deformation of the material occurs after the varnishing. The relatively thin layers which are formed by non-film-forming phosphatizing processes do not in this respect satisfy the practical requirements. These requirements with reference to zinc are admittedly better satisfied through chromate coatings, but the chromating processes have the disadvantage that large quantities of waste water must be decontaminated and these processes become, therefore, very expensive. Also even with chromate coatings, a better adhesion of the varnish and plastic layers is often desired. This happens particularly with the surface treatment of hot-galvanized steel.

Chromate coatings are generally applied to aluminum. These process conditions are, however, not suitable for applying of protective coatings onto iron and steel. The problem of treating steel and galvanized, especially Sendzimir-galvanized, surfaces and also aluminum surfaces with the same process often occurs in practice, particularly in strip operations. It is relatively expensive to introduce a special solution for each of the mentioned metals.

OBJECTS OF THE INVENTION

An object of the invention is the development of a process of coating diverse metals such as aluminum, iron and zinc under identical operating conditions using a complex fluoride coating solution.

A further object of the invention is the development

2

of a process for applying a protective coating on aluminum, zinc and iron under substantially identical operating conditions which consists essentially of applying to the metal surfaces of aluminum, zinc and iron of a complex fluoride coating solution free from chromic acid, phosphoric acid and oxalic acid having a concentration of from 0.1 to 15 gm. per liter, based on the metal content, of complex fluorides of metals selected from the group consisting of boron, titanium, zirconium and iron, from 0.1 to 10 gm. per liter of free fluoride ions and from 0.5 to 30 gm. per liter, calculated as sodium m-nitrobenzene sulfonate, of an oxidizing agent, at a pH of from 3.0 to 6.8 for a time sufficient to form a coating.

These and other objects of the invention will become more apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

The invention solves the problem of the development of a simple process for manufacturing of protective coatings on aluminum, iron or steel and zinc or zinc galvanized surfaces, which treats the different metal surfaces under identical operating conditions.

The new process is characterized in that the metal surfaces are treated until a coating has been formed with a solution, free of chromic acid, phosphoric acid and oxalic acid, which contains complex fluorides of boron, titanium, zirconium or iron in amounts of from 0.1 to 15 gm. per liter, calculated as the metal ion content, containing from 0.1 to 10 gm. per liter of free fluoride ions and 0.5 to 30 gm. per liter of oxidizing agents, calculated as sodium m-nitrobenzene sulfonate. The formed protective coating can eventually be after-treated with chromic acid and/or phosphoric acid containing solutions.

The application of solutions of complex fluorides of boron proved to be particularly suitable. They form especially hard and resistant coatings which represent, in addition to a good corrosion protection, an excellent adhering layer for varnish and plastic coatings, even where these coatings are later deformed, regardless of the metal coated.

The mentioned complex fluorides being utilized are water-soluble compounds which can be added directly into solution or which can be formed in the solution by addition of their components. The latter process can be carried out through addition of water-soluble salts of the metals as well as the corresponding amounts of fluoride ions. In this way, titanyl sulfate or zirconyl chloride can be utilized. The iron ions can be added, in addition to the complex fluoride as a water-soluble salt such as the sulfate, nitrate or chloride. The treatment solutions of this invention can also contain several of the metal ions or mixtures of different salts of the metals. If the fluoride ions are not added to the treatment solutions in the form of complex fluorides, then they are added as hydrofluoric acid or its neutral or acid salts. An excess of fluoride ions above the stoichiometrically required quantity for the forming of the complex fluorides is useful if the desired pH range is maintained. Preferably there is sufficient fluoride ions present in the coating solution to provide between 0.1 gm. per liter and 10 gm. per liter of free fluoride ions.

The solutions of this invention, as applied, contain an oxidizing agent, preferably sodium m-nitrobenzene sulfonate. Instead of the sodium salt, the free acid can also be utilized. By application of this oxidizing agent, it is possible to vary the treatment time of the metal surface to a very large extent. Instead of the m-nitrobenzene sulfonates, other oxidation agents can be used. Mainly such oxidation agents under consideration are those known as oxidizing acceleration agents for phosphatizing solutions, such as for example, alkali metal nitrates, nitrites, chlorates, bromates; hydrogen peroxide

and its addition products; aliphatic and aromatic nitro and nitroso compounds, such as nitroguanidine, picric acid, nitrophenols; as well as dinitrotoluene sulfonic acid and its alkali metal salts and quinone. Mixtures of different oxidizing agents can also be used. The oxidizing agents are preferably utilized in amounts of from 0.5 to 30 gm. per liter, preferably from 2 to 15 gm. per liter, calculated as sodium m-nitrobenzene sulfonate. In other words, if another oxidizing agent is utilized, it is used in amounts which would give an active oxygen release equivalent to the range of sodium m-nitrobenzene sulfonate.

Furthermore, it was found that the film forming can still further be accelerated by adding to the acid solutions, metal salts which form an insoluble oxide in the coating and which are between magnesium and hydrogen in the electromotive series. These are preferably water-soluble salts of zinc, nickel, cobalt and trivalent chromium. The amounts of these metal salts which are utilized amount to about 0.1 to 5 gm. per liter, preferably 0.2 to 2 gm. per liter, based on the metal salt added.

The treatment solutions must be practically free of chromic acid or chromium-(VI)-compounds, oxalic acids or oxalates and phosphoric acid or phosphates. These compounds or their corresponding anions interfere with the forming of the coating according to this invention, since they themselves are film-forming anions. Even relatively small quantities, for instance, of phosphates, decrease already the adhesion of varnish layers. Chromic acid and chromium-(VI)-compounds must moreover be excluded because of their poisonousness and the herewith connected expensive waste water purification.

The pH value of the acid solutions lies preferably in the range above 3.0 to 6.8. Optimum operating pH ranges and optimum spray times will vary depending upon the metal substrate and the selection of coating solutions in accordance with the invention. A pH range of 3.6 to 4.9 has been proven to be particularly suitable. The adjustment of the pH value can be carried out with alkalis or acids.

The treatment time is preferably short and amounts in general to 3 to 180 seconds, particularly 5 to 60 seconds. The treatment time is consequently so short, in strip installations with very high strip speeds, one can operate without the need for applying specially large baths or spraying zones.

The operating temperature of the acid solutions lies between 15° and 95° C., preferably between 40° and 65° C. The solutions can be applied with a dipping or brushing process; preferably, however, they are applied in a spraying process or by means of roll-coaters. The metal surfaces are cleansed or degreased before the treatment, according to this invention. This cleansing and degreasing can be carried out by means of solvents or with the customary alkaline; neutral or acid cleansers and depends upon the degree of soil.

In many cases it is advantageous to post-passivate the coatings obtained. This post-passivating can be carried out with a diluted solution of chromic acid and/or phosphoric acid or acid chromates and/or phosphates. The concentration of the chromic acid and/or the phosphoric acid or their salts lies generally between 0.01 and 5 gm. per liter.

A preferred execution form of the invention consists of the after-treatment of the protective coatings by means of diluted chromic acid which contains chromium-(III)-ions. The concentrations applied lie generally between 0.2 and 3 gm. per liter CrO_3 and 0.05 to 1 gm. per liter Cr_2O_3. Subsequent to the post-passivating the coatings are dried. Before the after-treatment the metal surfaces are rinsed appropriately with water, although this rinse is not absolutely necessary, particularly if one operates with suitable squeeze rollers. The after-treatment can, if desired, be varied depending upon the kind of metal surface. The amounts of chromic acid solutions which eventually collect by the after-treatment are small in comparison to the customary chromating processes and can easily be reduced in batches, so that no waste water difficulties arise.

The treatment baths of the invention can be prepared through dissolving the above-stated compounds or through diluting of corresponding concentrates. They can be used during long periods of time and can again and again be replenished to constant points with the starting materials. The points of a solution are hereby defined in the customary way as the amount in ml. of 0.1 N NaOH which is necessary to titrate 10 ml. of bath solution to the turning point of bromophenol blue (free acid) or phenolphthalein (total acid). An additional pH correction may be necessary after replenishing several times if the baths are replenished with the same liquid or solid concentrates.

For this reason the baths are preferably replenished with solutions or concentrates, which contain complex fluorides of boron, titanium, zirconium and/or iron and at least one oxidizing agent and which have an acid ratio of free acid to total acid of 1:1.05 to 1:5.0, preferably 1:1.5 to 2.5.

The process of the invention produces on aluminum, iron or steel, zinc and zinc galvanized surfaces, evenly thin, easily deformable, homogeneous coatings which give a good corrosion protection and possess an excellent varnish adhesion. The coatings on steel are mouse-grey to bluish iridescent, those on zinc and aluminum, dull-light-grey to light yellowish iridescent. The process can easily be maintained, and the baths possess a very long life. The same baths can be used under equal operating conditions for all of the mentioned metal surfaces.

The following specific embodiments are illustrative of the invention without being limitative in any respect.

Example 1

In a spraying installation protective coatings were successively applied to steel strips, Sendzimir-galvanized steel strips as well as to aluminum strips. The strips were first degreased with alkali, rinsed with cold water and subsequently treated with a solution of the following composition:

	Gm./liter
$Na[BF_4]$	1.5
$NaNO_3$	4.0
Sodium m-nitrobenzene sulfonate	4.5
$Zn(NO_3)_2 \cdot 6H_2O$	0.2

The pH value was adjusted to 6.6. The treatment temperature amounted to 35° C. and the treatment time to 120 seconds. The treated strips were rinsed subsequently with cold water and post-passivated for 6 seconds with a solution which contained, in the case of the steel strips, 0.1% by weight of NaH_2PO_4 and, in the case of the Sendzimir-galvanized strips, 0.02% by weight of chromic acid. Thereafter they were dried.

The layer-forming treatment solution was, however, the same for all strip types. Thin, evenly good, deformable coatings with excellent adhesion for paint and plastic were obtained with this treatment solution on aluminum and on Sendzimir-galvanized material as well as on steel.

In changing from zinc to steel surfaces or to aluminum surfaces neither the bath composition nor the operating conditions, such as for instance, the transporting speed (treatment time), pH value and bath temperature, had to be changed.

Example 2

Equally good results were obtained following the process of Example 1 in using a solution of the following composition instead of the treatment solution mentioned in Example 1:

	Gm./liter
$(NH_4)_2[ZrF_6]$	1.5
$NaNO_3$	26.0
$Co(NO_3)_2 \cdot 6H_2O$	0.5
Sodium m-nitrobenzene sulfonate	1.0

The pH value amounted to 5.2, the treatment temperature to 70° C., and the treatment time to 30 seconds. Below 70° C., for instance, at 55° to 65° C. and at exposure times of 20 to 60 seconds, coatings of the same good quality were obtained.

Example 3

In a spray installation coatings were applied successively to sample strips of steel, galvanized steel and aluminum respectively. In each case the metal strips were degreased and cleaned with a conventional alkaline cleaner, rinsed with cold water and then sprayed with a solution of the following composition:

	Gm./liter
Zinc fluoborate	30.0
Sodium nitrite	0.37
Ammonium fluoride	4.0

Sodium hydroxide, added as necessary to adjust pH to 4.3 to 4.9.

The treatment temperature was maintained at approximately 65° C. and after treatment the metal strips were rinsed with cold water and post-passivated with chromic acid solution (0.06 percent by wt. chromium-IV-ions and 0.02 percent by wt. chromium-III-ions) and thereafter dried. The time of spray treatment was varied, with corresponding variations in coating weight. A 60-second spray on steel gave a coating of 0.83 gm./meter^2. A 60-second spray on galvanized steel gave a coating weight of 2.1 gm./meter^2 and a 60-second spray on aluminum gave a coating weight of 2.4 gm./meter^2. In all cases the coating was of a light gray amorphous appearance, uniform and evenly distributed with excellent adhesion for paint and excellent corrosion resistance properties.

On continued bath loading, the coating solution was replenished with zinc fluoborate so as to maintain the zinc concentration above 4.0 gm./liter and preferably above 10 gm./liter. Alternatively the coating solution may be replenished by adding zinc oxide and fluoboric acid thereto to produce zinc fluoborate in situ. The fluoride activity of the bath should be maintained at a concentration equivalent to 2.0 gm./liter of fluoride ion or greater by the addition of ammonium fluoride as necessary. The nitrite concentration is preferably maintained at 0.25 gm./liter calculated as nitrite, or greater. The pH is preferably maintained between about 4.3 and 4.9 by the addition of sodium hydroxide.

The addition of zinc fluoborate can be conveniently controlled by conventional zinc titration techniques customarily employed in producing zinc phosphate coatings on metal. The fluoride ion content can be conveniently controlled by use of electronic equipment, such as the commercially available Lineguard Meter No. 101A (described in United States Patent 3,350,284). Nitrite concentration is conveniently controlled by conventional titration methods, such as a potassium permanganate titration conventionally employed in metal coating processes utilizing nitrite as an oxidizing agent.

The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the art may be employed without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. A process for applying a protective coating on aluminum, zinc and iron under substantially identical operating conditions which consists essentially of successively applying to the metal surfaces of aluminum, zinc and iron of a complex fluoride coating solution free from chromic acid, phosphoric acid and oxalic acid having a concentration of from 0.1 to 15 gm. per liter, based on the metal content, of complex fluorides of metals selected from the group consisting of boron, titanium, zirconium and iron, from 0.1 to 10 gm. per liter of free fluoride ions and from 0.5 to 30 gm. per liter, calculated as sodium m-nitrobenzene sulfonate, of an oxidizing agent, at a pH of from above 3.0 to 6.8 for a time sufficient to form a coating.

2. The process of claim 1 wherein said complex fluoride coating solution is applied to said metal surfaces for a period of from 3 to 180 seconds.

3. The process of claim 2 wherein said application period is from 5 to 60 seconds.

4. The process of claim 1 wherein said pH is from 3.6 to 4.9.

5. The process of claim 1 wherein said complex fluoride of metals is a complex boron fluoride.

6. The process of claim 1 wherein said complex fluoride coating solution has a content of from 0.1 to 5 gm. per liter of a soluble metal salt of a metal which in the electromotive series lies between hydrogen and magnesium and which forms an insoluble oxide.

7. The process of claim 1 wherein said complex fluorides of metal is from 0.1 to 15 gm. per liter of zinc fluoborate, calculated as boron.

8. The process of claim 7 wherein said zinc fluoborate is produced in situ by zinc oxide and fluoboric acid.

9. The process of claim 7 wherein said pH is from 4.6 to 4.9.

10. The process of claim 1 wherein said oxidizing agent is sodium m-nitrobenzene sulfonate.

11. The process of claim 1 wherein said oxidizing agent is sodium nitrite.

12. The process of claim 1 wherein said coated metal surfaces are post-passivated by application thereto of a dilute chromic acid solution containing chromium-III ions.

13. The process of claim 1 wherein said complex fluoride coating solution is continuously applied to continuously moving metal surfaces and said coating solution is continuously replenished with concentrates of its constituents having an acid ratio of free acid to total acid of 1:1.05 to 1:3.

References Cited

UNITED STATES PATENTS

3,539,402	11/1970	Ries	148—6.2 X
3,539,403	11/1970	Ries	148—6.2 X
2,332,487	10/1943	Loose	148—6.27 X
1,638,273	8/1927	Pacz	148—6.27
1,710,743	4/1929	Pacz	148—6.27
3,066,055	11/1962	Pimbley	148—6.14 X
2,276,353	3/1942	Thompson	148—6.2
2,357,219	8/1944	Mott	148—6.14 R
3,160,506	12/1964	O'Connor et al.	148—6.2 X

RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

148—6.27, 6.15 R, 6.16, 6.2